One-Step Production of Monolith-Supported Long Carbon Nanotube Arrays

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Abstract

Aligned carbon nanotube (CNT) arrays over 150 μm long have been grown by catalytic chemical vapour deposition on the walls of bare cordierite monoliths in a single step. The method described avoids the need for the multiple pre-treatment steps currently applied, and is coupled with an increase in the thickness of the carbon layer obtained by an order of magnitude compared to literature. Uniform CNT growth has been obtained over different lengths of monolith. The resulting CNT/cordierite monoliths have a high surface area and low pressure drop, making them a viable support for use in industrial catalysis.

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1. Introduction

Structured catalyst supports or monoliths have clear advantages over traditional powder catalysts when used in large-scale reactors [1], including lower pressure drop and better control of heat and gas flow, giving uniform flow distributions and residence times [2, 3]. Monoliths are typically made of ceramics, metals or carbon and contain small diameter (0.5-4 mm), uniform channels [3]. Ceramic monoliths like cordierite are commonly used in catalytic converters as the support material. As well as catalytic converters, monolithic reactors have been used in a range of reactions, including NO*x* conversion with ammonia for large-scale applications [4, 5], the Fischer-Tropsch process [6, 7], synthesis of hydrogen from ammonia [8], hydrogenation of unsaturated bonds in a number of species [9], steam methane reforming [10] and biodiesel synthesis [11].

A major limitation of monoliths as catalyst supports is their very low surface area, with a typical bare cordierite monolith having a surface area of about 0.7 m^2g^{-1} [1]. In order to overcome this problem, monoliths are coated with a thin layer of a high surface area material to allow higher loadings of catalyst onto the support. Commonly, an alumina or silica slurry coating is applied onto the monolith, with the increase in surface area dependant on the thickness of the applied wash-coat, resulting in values of up to 15-30 m^2g^{-1} for 0.1-50 μm thick coatings [12, 13]. However, these coatings increase the pressure drop across the monolith, partially reducing their advantage over packed bed configurations. In addition, achieving a uniform wash-coat on a large scale can be problematic [13].

To further increase the surface area of wash-coated monoliths, growth of carbon nanotube (CNT) or carbon nano-fiber (CNF) forests on the surface of the wash-coat layer has been proposed [12, 14, 15]. Some of these carbon layers have been shown to double the surface area of the wash-coated monoliths [12]. CNTs and CNFs have been chosen as they have shown promise as catalyst supports with high absorption properties, controllable mesoporosity and specific metal support interactions, yielding improved catalytic activity and selectivity [16]. However, these fine and light powders can be difficult to handle. In order to utilise these powders in industrial scale reactors they must be compressed and extruded into a new structure in a multi-step process with the CNT powder being difficult to compress into a pellet using standard methods [17]. The potential health problems associated with handling powdered CNTs could also limit their utilization in industrial environments [16]. Coating a monolith with CNTs offers a safer and more practical solution to both issues, providing a CNT support with lower pressure drop directly upon synthesis without the necessity of subsequent treatment whilst the strong adhesion between the monolith surface and the CNTs makes it unlikely that the CNTs will become airborne [18].

Typically, CNTs/CNFs are grown on monoliths *via* catalytic chemical vapour deposition (cCVD). This process requires a second pre-treatment of the monolith (after the wash-coating step) consisting of the impregnation with a catalyst, usually iron-, cobalt- or nickel-based, to initiate growth of the carbon layer [12, 18, 19]. The thickness of the alumina wash-coat layer was found to be an important factor in the growth of the CNF layer. If the alumina layer was less than 0.1 μm, the distribution of the alumina wash-coat was non-uniform, and growth of the carbon layer was similarly uneven [12]. When the alumina layer was thicker (~17 μm) the thickness of the CNF

layer grown was smaller, suggesting that some of the CNFs were embedded within the porous alumina [15]. Further studies have shown that a thin wash-coat is considered desirable for the growth of the CNF layers, with a 0.1 μm thick alumina layer being reported as optimal [12]. Even under this optimal condition, though, the CNF layers produced are thin and poorly aligned [12, 14].

In this work, CNT growth directly onto the surface of an untreated cordierite monolith, avoiding the necessity of any pre-treatment step is reported. The uniform cordierite surface enables the formation of long, highly aligned arrays of CNTs on the surface of the monolith, as opposed to the disordered CNF layers formed when an alumina wash-coat is used. Ferrocene has been used to catalyse the formation of CNTs on the surface of the monoliths, with various growth conditions tested to assess changes to the CNT layer properties.

2. Experimental

2.1 Preparation of CNT composites

The cordierite monolith (Dow Corning, 1.1 mm square channels, 62 cells/cm^2, 1 cm diameter cylinders with varying lengths) was placed in the centre of a quartz reactor (1 m × 2 cm outer diameter tube). The monolith was heated under an argon atmosphere (50 sccm/min argon, 5 °C/min) until the reaction temperature was reached. Once the growth temperature was reached (730-850 °C, typically 790 °C), the flow of argon was increased to 450 sccm/min, and 50 sccm/min of hydrogen were introduced to the system. Then a solution of toluene and ferrocene (0.1 M) was injected into the first zone of the furnace at 300 °C (10 mL/hr constant flow rate) using a syringe pump for the length of the reaction run (15-120 minutes, typically 60

min), ensuring that the concentration of both ferrocene and toluene is not limiting growth. After the reaction, the system was cooled to room temperature under a flow of argon (50 sccm/min).

2.2 Characterization

CNTs were characterised using a transmission electron microscope (TEM, JEOL 1200) operated at 200 kV. Samples for TEM analysis were mechanically detached from the monolith, dispersed in ethanol and deposited onto Cu or Ni grids. Scanning electron microscopy (SEM) was carried out using a JEOL SEM 6480LV operating at 5 - 20 kV. Raman spectra of the CNTs were recorded from 1000-3000 cm^{-1} using a Renishaw Invia system equipped with an 830 nm laser. Raman spectra were taken by dropping detached CNTs in ethanol onto a silica plate, or directly from the CNT layer on the monolith. Temperature programmed oxidation (TPO) experiments were carried out in a thermo-gravimetric analyser (TGAQ500, TA-instruments). The temperature ramping was 5 °C/min from room temperature to 900 °C in 100 ml/min of air. Axial crushing strength was determined using an Instron 3369. A square monolith piece (0.6 cm × 0.6 cm) was placed under a 1 kN load and the pressure was slowly increased until the wall crumpled. The measurement was repeated five times to ensure accuracy. BET specific surface areas (N_2, 77 K) were obtained from low pressure (up to 1 bar) nitrogen sorption measurements at 77 K using a Micrometrics ASAP 2020 volumetric gas sorption analysis system. The specific surface area was calculated according to the British Standard guidelines for the BET method from regression analysis of data in the relative pressure range from 0.05 to 0.3[20]. Samples were degassed at 200 °C under dynamic vacuum for 12 hours prior to analysis.

3 Results and Discussion

3.1 Effect of Substrate on CNT Growth

Significant differences in CNT growth (in terms of length and alignment) can be observed for the bare and alumina wash-coated cordierite (Fig. 1). In particular highly aligned CNT arrays over 100 μm in length can be observed on the bare cordierite (Fig. 1 c, e and g). On the other hand, for the same growth conditions, random orientation CNT growth has been observed on the alumina wash-coated cordierite (Fig. 1 d, f and h), in agreement with literature results [8, 12, 15]. CNT lengths observed on this alumina wash-coat are longer than those reported in the literature, but equally non-aligned, and non-uniform [8, 12, 15]. This significant improvement over published results is attributed to the particular growth method used in this work, combined with the different surface structure of the two supports. As discussed earlier, this is based on an aerosol-assisted CVD process where the ferrocene catalyst and the toluene carbon source are introduced into the reactor simultaneously [21, 22]. This method allows the uniform deposition of iron nanoparticles onto the bare monoliths which have a more uniform surface with lower surface area [21] compared to the wash-coated monoliths. The aerosol method does not rely on the higher surface area provided by an alumina wash-coat to achieve sufficient dispersion to produce nanoparticles, as is the case for the incipient wetness techniques used previously in the literature [12, 21]. For the highly porous wash-coated alumina system, catalyst particles were deposited within the porous material. As a result, CNT growth occurs in all directions normal to the porous surface resulting in the disordered layer of CNTs observed (Fig. 1h).

For the relatively non-porous bare cordierite, most nanoparticles deposit on the walls of the monolith. As can clearly be seen from Fig. 1 c, e and g, this results in a highly ordered structure, with CNT growth naturally oriented perpendicular to the surface. As all the CNTs grow in the same direction, the CNTs support each other, with ordered bundles observed (Fig. 1g and Fig. S1).

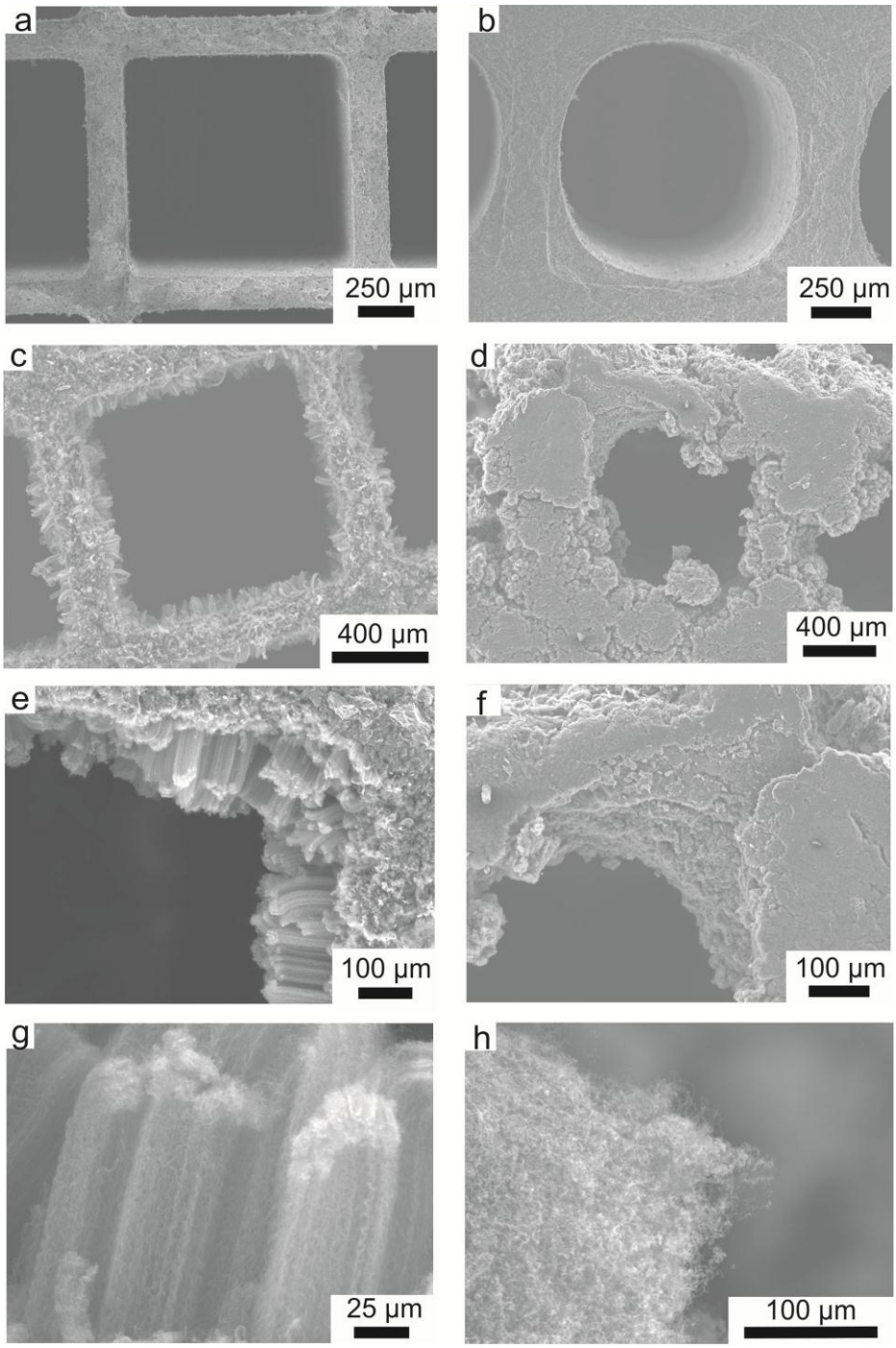

Fig. 1 - SEM micrographs of a) bare cordierite monolith and b) alumina wash-coated cordierite monolith before coating with carbon. The differences in growth observed on bare and wash-coated monoliths is shown, with c) e) and g) showing ordered uniform growth on bare cordierite at different magnifications, whilst d)

f) and h) show disordered growth on alumina wash-coated cordierite at increasing magnification.

Raman spectroscopy and TEM analysis has confirmed the presence of long multi-walled CNTs (average diameter 40-80 nm) grown on the bare cordierite (Fig 2). A relatively high I_D/I_G ratio (~2) suggests that the CNTs formed contain a significant number of defect sites (Fig. 2c, curve 1) [23]. The CNTs also contain significant amounts of iron in their core but not outside (Fig. 2b). Oxidation in air at 550 °C for 20 minutes was used to open the CNTs caps, without significantly altering other aspects of the CNT structure (Fig. 2b-c, curve 2) or removing the iron inside the CNT core (Fig. 2b). It should be noted that the presence of defects on the CNTs can be beneficial to their use as catalyst supports as it has been shown that catalyst particles deposit preferentially on defect sites of untreated CNTs [16].

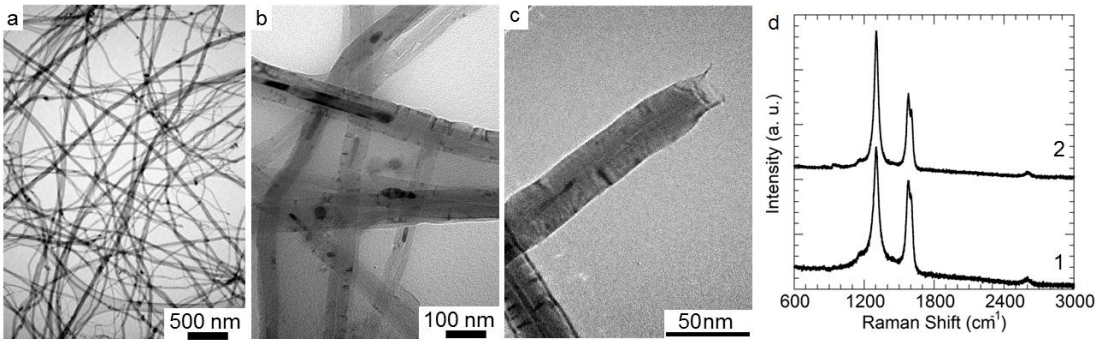

Fig. 2 - TEM micrographs of a) as produced CNTs and b) after oxidation in air at 550 °C for 20 minutes; c) open CNT end after oxidation in air at 550 °C for 20 minutes; d) Raman spectra of CNT grown on (1) bare cordierite monolith at 790 °C and (2) after oxidation in air at 550 °C for 20 minutes.

3.2 Effect of time and growth temperature on thickness of the carbon layer

Analysis of SEM micrographs taken of the CNT layer show that thickness increases with the growth time on the bare cordierite surface at all temperatures tested (Fig. 3). The maximum thickness of the carbon layer observed is at 790 °C after 90 minutes, with a thickness of 160 μm. This is significantly greater than that of those grown at higher and lower temperatures, 730 and 850 °C, which result in maximum carbon layer thicknesses of 47 and 89 μm, respectively. This indicates that 790 °C is in the optimum temperature range for CNT growth on this substrate. At 790 °C a maximum thickness is achieved after 90 minutes. It appears that further growth of the carbon layer is hindered or significantly slowed from this point on, as after 2 hours the thickness of the carbon layer has not increased further. The slowdown is to be expected due to several reasons[24] [25]. In particular, it can be attributed to diffusion limitations through a thick CNT layer associated with the base growth model [26]. This effect is not as pronounced for the thinner layers produced at 850 and 730 °C. TGA analysis shows similar trends with carbon wt% increasing with time, and 790 °C being the optimum growth temperature (see Fig. S2, supporting information). It is to be noted that no slowdown is observed in the carbon wt% change data, suggesting that beyond 90 minutes further CNT growth results in a denser layer of CNT rather than a thicker one.

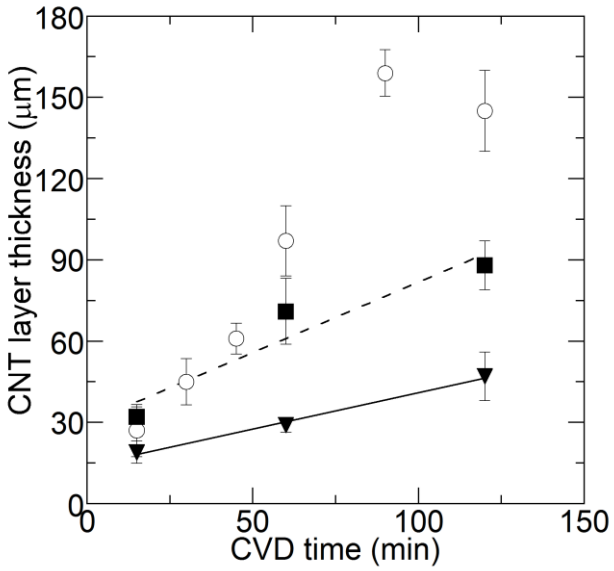

Fig. 3 CNT layer thickness as a function of CVD growth time at (▼, —) 730 °C, (○) 790 °C. and (■, ---) 850 °C. The CNT layer thickness was determined from image analysis of SEM micrographs of the CNT layers 100 μm long at 10 μm intervals; error bars represent one standard deviation.

The carbon layer thickness is significantly greater than those reported previously on this same support using a nickel (4 μm thickness after 220 minutes at 650 °C) or cobalt (0.6 μm thickness after 20 minutes at 730 °C) catalyst [12]. Even at 730 °C, where growth is significantly less than at higher temperatures, the carbon layer thickness of 19 μm after 15 minutes, and 47 μm after 120 minutes is still an order of magnitude greater than those previously reported. The use of a ferrocene/toluene mix, which continually provides fresh catalyst precursors into the system, has been suggested as a possible reason for the high growth rates observed in similar methods [27].

Temperature programmed oxidation (TPO) experiments confirm the presence of a thicker carbon layer at 790 °C with a higher peak compared to the other growth temperatures due to the presence of a higher wt% of carbon (Fig. 4a). It appears that growth temperature does not affect the quality of the CNTs formed significantly. TPO confirms the similar behaviour of the CNT/monolith with oxidation beginning at the same temperature for CNT produced at all temperatures. Raman spectra observed for each synthesis temperature, have similar I_D/I_G ratios of 1.9 for CNT produced at 730 and 790 °C, and 2.3 for CNT produced at 850 °C (Fig. 4b). Both analyses indicate the production of graphitic CNTs, with CNT produced at 850 °C being slightly more defective.

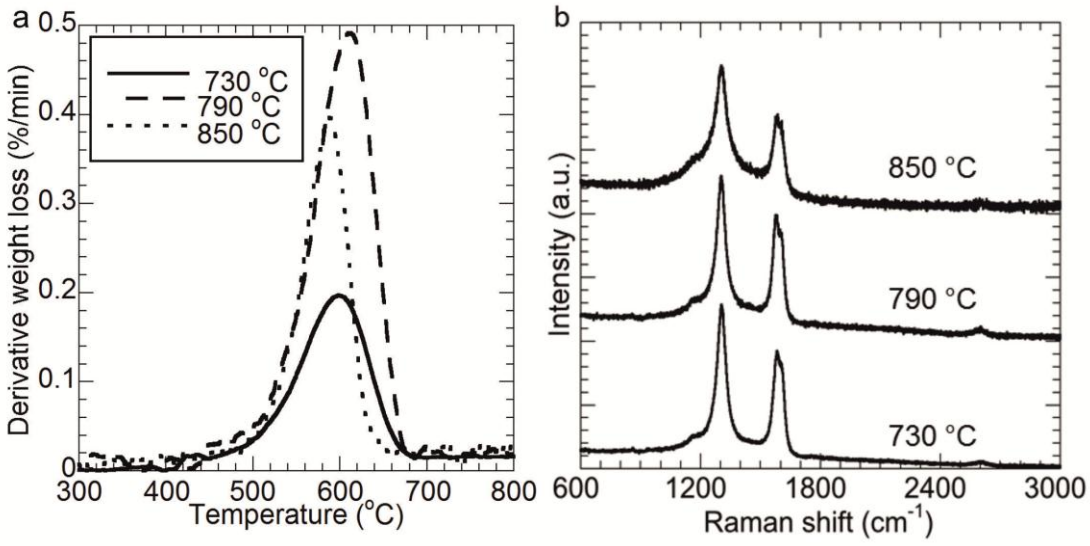

Fig. 4 - a) Derivative of the weight loss in temperature programmed oxidation experiments of the CNT composites after 60 minutes growth at different temperatures. b) Raman spectra of the CNT composites after 60 minutes growth at different temperatures.

Mechanical testing of the monoliths indicated that the monolith strength has been retained, with the axial crushing strength equal or slightly higher after CNT growth (Table 1). On the other hand, wt% CNT loading and coating thickness on the monolith are strongly affected by the growth temperature (Table 1). Previous authors have observed total collapse of monoliths [12, 15] under conditions where growth is extremely fast. Generally this behaviour is not observed in our samples, though collapse of the monolith samples has been observed for a few samples grown at 790°C or higher for longer than an hour. In the literature, this collapse is attributed to damage caused by growth of CNTs within the macroporous structure of the monolith [15]. In our case, though, few nanoparticles deposit within the macropores, therefore this collapse is rarely observed. Likewise, we observed no cracks in the monolith wall as observed by Jarrah *et al*. [15] Analogous trends have been observed for the wash-coated monoliths tested.

The adhesion of the CNTs to the monolith was evaluated in two ways: First, following literature procedures [8, 14, 28], the 790 °C CNT/cordierite composites were subjected to extended maltreatment via sonication in ethanol at 37 KHz, for 30, 60, 120 and 180 minutes. CNT mass decreased from 4.5 wt % to 3.6 wt % of the composite in the first 30 minutes, after which no further loss of CNTs was observed. This loss is slightly higher than that observed by previous authors, who have suggested that growth of CNF into the macroscopic structure of the cordierite from the alumina wash-coat is the reason for this strong attachment [8, 14, 28]. As discussed previously, in our case this effect would be unlikely to occur, as the attachment of the CNT to the substrate probably occurs through a nanoparticle at the base of the CNT, anchored to the cordierite. Additionally the entangled bundles of

CNT could be expected to support each other, increasing attachment (Fig. S1). A second method, closer to actual experimental conditions, was to place the CNT/cordierite monolith in a reactor under a flow of gas, similar to that used in a FT reaction (100 ml/min for 32 hours). At the end of the reactor a filter paper was placed to collect any CNT detached from the monolith. No loss of CNT was visible after 32 hours.

Table 1. Characterization of CNT coating of the composite monoliths at different temperatures after 60 minutes

Growth Temperature (°C)	CNT weight per monolith (%)	Average coating thickness (μm)	Axial Crushing Strength (MPa)*
730	2.4	29±3	54±4
790	4.5	97±13	55±4
850	4.4	71±12	58±8

* Bare monolith gave axial crushing strength of 49±6 MPa

3.3 Surface area of the CNT layer

The surface area of the 790 °C CNT/cordierite monolith after 60 minutes growth is about 4 m^2g^{-1}. Heating in air at 550 °C for 20 minutes removes any remaining amorphous carbon and opens the ends of the CNTs, leading to a doubling of the surface area to 8 m^2g^{-1}, without significant damage to the CNTs (Fig. 2c). This corresponds to an order of magnitude increase from the 0.7 m^2g^{-1} value of the bare cordierite. It is nonetheless significantly lower than values previously reported of 30 m^2g^{-1} and 63 m^2g^{-1} for CNT/CNF layers grown on alumina wash-coated monoliths [8, 12, 28]. This difference can be attributed to several factors: First, the alumina wash-coat accounts for a significant percentage of the surface area of the CNT/CNF-wash-coated monolith with approximately 50% of the surface area coming from the wash-

coat for the 30m^2g^{-1} samples, and over 70% for the 63 m^2g^{-1} ones. Secondly, the CNT powder obtained under the same conditions on quartz has a relatively low surface area (~35 m^2g^{-1}) due to the relatively large diameters of the CNTs produced (~50 nm) contributing to the low overall surface area values obtained from the composites. Finally, the synthesis method used here results in capped CNTs with a significant amount of iron in their core (Fig. 2b). As discussed previously, oxidation at 550 °C in air opens the caps, increasing the surface area. Removal of iron from oxidized CNTs (produced using the same method but on a quartz support) *via* hydrochloric acid treatment (24h reflux in concentrated HCl) effectively doubled the CNTs surface area from 35 m^2g^{-1} to 62 m^2g^{-1}. Unfortunately, the same process applied to the CNT/cordierite results in the deterioration of the cordierite support.

3.4 Potential for scale up

Growth of CNTs has been successfully achieved on monolith pieces 1 cm long and 1 cm in diameter. For a potential scale up of this process to industrial level it is necessary to determine whether uniform growth of CNTs across longer monolith pieces is possible. Analysis of an optical micrograph of a typical 9 x 1 cm CNT/cordierite monolith piece with SEM and Raman measurements taken along this monolith demonstrates the presence of CNTs across the longer monolith piece with uniform length and morphology consistent with results for the shorter samples (Fig. 5). This confirms that growth can be achieved on longer monolith pieces, and that this process can produce the CNT/cordierite composites on the larger scale necessary for industrial catalysis. We attribute the homogenous deposition of CNTs on the

monolith within the reaction zone to the excess of ferrocene and toluene coupled with the high flow rate.

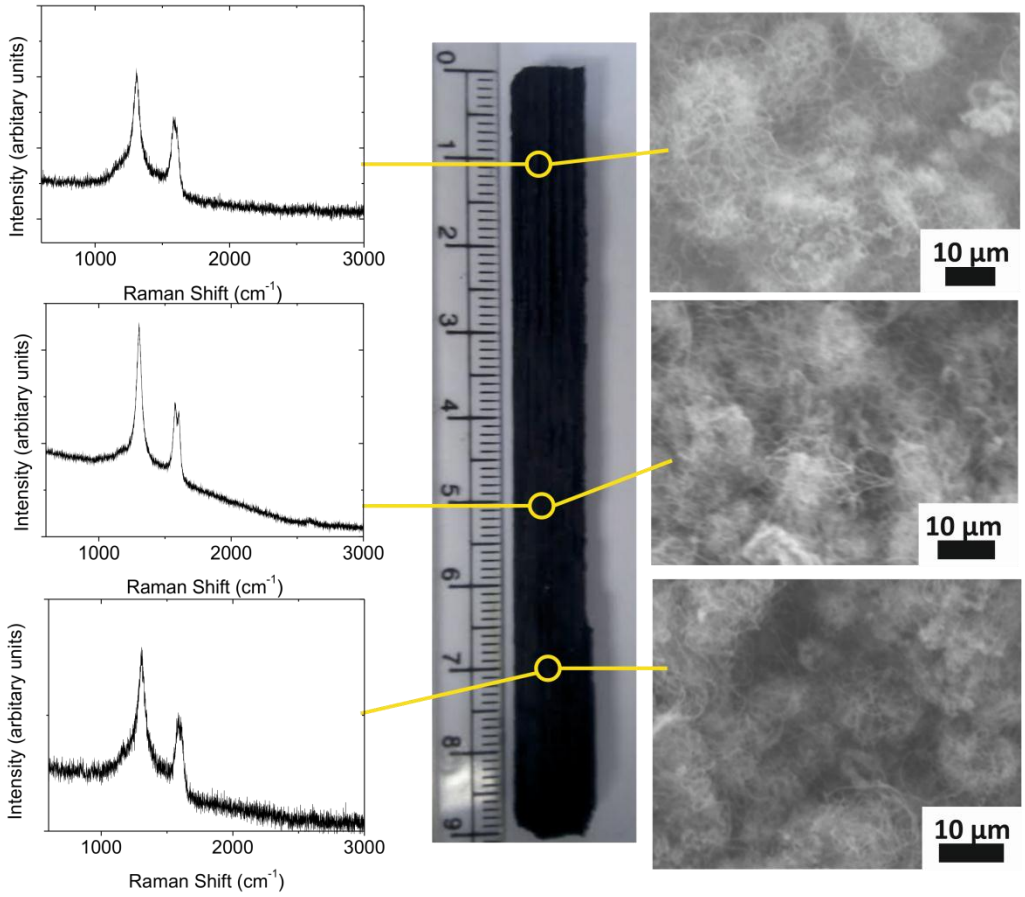

Fig. 5 Optical micrograph of cross-sectioned 9 x 1 cm CNT coated cordierite monolith with SEM micrographs and Raman spectra showing uniform coverage by CNTs

A key advantage of monoliths compared to packed bed reactors is a low pressure drop, which can be important in large scale reactions. In Fig. 6 a comparison between 10 cm long × 1 cm diameter bare cordierite monoliths, wash-coated alumina monoliths, CNT coated monoliths and an equivalent amount of CNT in a packed bed configuration (0.1 g, roughly equivalent to the weight of CNT grown on the coated

monoliths) is shown. It can be clearly seen that the equivalent amount of CNT has a very high pressure drop in comparison to all monoliths, as would be expected due to the lack of open space for gas to flow through. The difference in pressure drop between the bare cordierite and the CNT coated monolith is negligible, despite the additional volume occupied by the CNT layer. However, the wash-coated monolith has approximately double the pressure drop than the CNT-coated monolith for the same free cross-sectional area (0.65 mm^2 and 0.64 mm^2, respectively). No significant difference was observed between a single 10 cm long monolith and 10 × 1 cm long monoliths occupying the same reactor section.

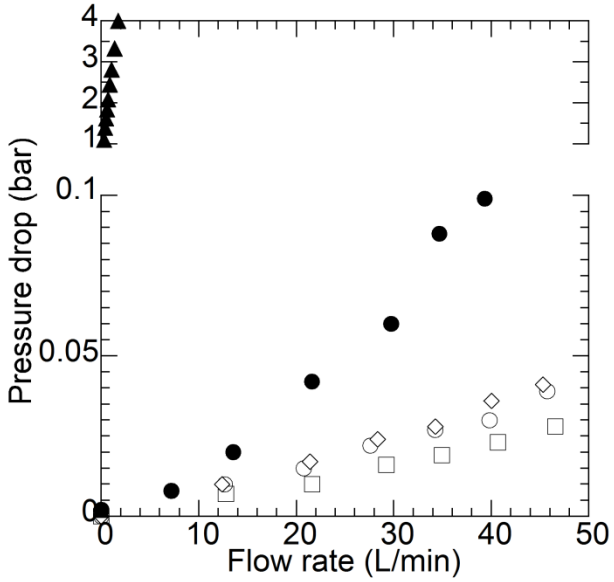

Fig. 6 - Pressure drop over a 10 cm × ½ inch Swagelok™ tube filled with: (○) 10 × 1 cm bare cordierite monolith; (◊) 10 × 1 cm CNT coated cordierite monolith; (●) 10 × 1 cm alumina wash-coat cordierite monolith; (□) empty reactor tube; and (▲) equivalent mass of CNT powder in packed bed configuration.

4. Conclusions

CNTs have been successfully grown onto the surface of a bare cordierite monolith in a one step process, avoiding multiple pre-treatment steps previously reported as necessary. Using an iron-based catalyst instead of a nickel system, aligned arrays of CNTs up to 150 μm in length have been produced. The thickness of the CNT layer can be further increased by increasing the deposition time and synthesis temperature, with the optimal conditions found to be 90 minutes at 790 °C. While the surface area values obtained are lower than comparable wash-coated monoliths, a significantly lower pressure drop is obtained here compared to the former, making these supports suitable for large scale catalysis applications. Surface area has been further increased by a partial oxidation in air of the CNT caps, yielding a one order of magnitude increase compared to the bare monolith. Scalability of the process has been shown with uniform CNT growth for 1 and 10 cm long monoliths.

Acknowledgements

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